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Preparation and characterisation of Pd–TiO_2–hydroxyapatite nanoparticles for the photocatalytic degradation of cyanide under visible light

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ABSTRACT

Hydroxyapatite nanoparticles were successfully synthesised by an ultrasonic irradiation method. Pd–TiO_2–hydroxyapatite nanoparticles with 3 wt% of Pd and 25 wt% of TiO_2 were successfully synthesised by an impregnation method. For comparison, Pd–TiO_2 (3 wt% Pd) has been also synthesised by an impregnation method. The catalytic performance was evaluated by photocatalytic oxidation of cyanide under visible light irradiation. Extended X-ray absorption fine structure (EXAFS) measurements revealed the presence of the peaks assigned to the Pd–Pd bond at approximately 2.54 Å. Terephthalic acid assay confirmed formation of hydroxyl radicals in cyanide solution treated with photocatalysts and the amount of the formed hydroxyl radials in the case of Pd–TiO_2–hydroxyapatite nanoparticle is the highest than that of Pd–TiO_2 and TiO_2 nanoparticles. The improved photocatalytic activity of the Pd–TiO_2–HAP systems is due to the absorption of radiation in the visible light region, the small recombination rate of the electron–hole pair, and the high surface area. The photocatalytic degradation of cyanide was found to follow first-order kinetics. Recycling experiments confirmed the relative stability of the catalyst.

1. Introduction

Cyanide originates from metal finishing, ore extraction, and hydrometallurgical industries. It is used in the production of organic chemicals such as nitrile, nylon, and acrylic plastics. Other industrial applications utilising cyanide include electroplating, metal processing, steel hardening, and synthetic rubber production. Many common plants contain the natural form of cyanide, cyanic glucoside. Its presence may be the product of evolution, as it deters animals and insects from consuming the entire plant. Most animals can tolerate digesting small amounts of cyanic glucoside, but during a drought, the amount of the chemical in plants increases. As a result, animals could poison themselves by eating plants with high concentrations of cyanic glucoside. The traditional treatment method of cyanide is the chlorination of cyanide, but the drawback of this method is the production of cyanogens gas (CNCl), a known carcinogen. The produced gas is poisonous, harmful, and essentially causes environmental pollution that requires further treatment. Heterogeneous photocatalysis could be conducted on gas phases, pure organic liquid phases, or aqueous solutions.

Photocatalysis is the method of choice used professionally for the treatment of polluted water. Currently, the TiO_2 photocatalyst is most commonly used for the removal of pollutants [1–3]. Because photocatalytic reactions occur on the surface of TiO_2, the enhancement of its photocatalytic activity can be achieved by either the alteration of the surface properties of the catalyst itself [4–7] or the immobilisation of the catalyst onto a substrate that improves its surface properties [8–17]. The substrate needs a large surface area for more of the catalyst to be involved in photocatalytic reactions and to easily allow the mass transfer of the pollutant and degraded products. The supporting material should have a definite affinity for pollutants to provide efficient trapping and degradation. The substrate material should be transparent or semitransparent to allow UV and visible radiation to pass through it and the superior surface of the catalyst to be activated. A plethora of materials that partially or completely satisfy the demands mentioned above were investigated: porous inorganic minerals such as zeolite [8], pumice stone [9], and mordenite [10]; adsorbent support materials such as activated carbon powder [10], fibres [11], or nanotubes [12]; co-catalysts such as graphene [13]; and transparent supports such as porous silica [10,14], glass fibres [15], beads [16], and springs [17].Hydroxyapatite (HA) is a good supporting material due to its transparency and excellent adsorption

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properties towards different aqueous and air pollutants [18–21]. Thus, HA has been utilised for removal of heavy metals from water [19,20]. HA-coated organic substrates showed high adsorption for damaging VOCs such as formaldehyde [21]. HA was also used as an NO_2 collector [18]. HA exhibits photocatalytic activity [22–26] during the decay of several toxic organic compounds in an aqueous solution or in a gaseous phase. Photocatalytic decay over HA showed good results for methylene blue [22], methyl mercaptan [23,24], dimethyl sulphide [25], and azo dyes [26]. It was suggested that the photocatalytic activity of HA is caused by the generation of active superoxide anion radicals ($O_2\bullet^-$) due to a change in the electronic state of the surface $PO_4{}^{3-}$ group under UV irradiation [23–26]. There are also some examples of the usage of HA/TiO_2 composites where the adsorption properties of HA are joined with the photocatalytic properties of TiO_2 [18,22,27,28]. Thus, the decay of methylene blue [22] and methylene orange [28] on HA/TiO_2 particles was much quicker than on HA/TiO_2 powder alone. This was the result of the strong adsorption of the reaction intermediates on HA and their subsequent transfer to TiO_2. The HA/TiO_2 film showed a better decay effect on formaldehyde gas compared to bare TiO_2 due to the synergistic effect of the high photocatalytic activity of TiO_2 and the high adsorption ability of HA [27].

This study synthesised Pd–TiO_2–hydroxyapatite nanoparticles (Pd–TiO_2–HAP) using a template-ultrasonic assisted method and then assessed the materials for enhanced adsorption and photocatalytic performance. The photocatalytic activities were measured by photocatalytic removal of cyanide under visible light irradiation.

2. Experimental

2.1. Preparation of hydroxyapatite

The preliminary materials used in the synthesis of nanohydroxyapatite (HAP) include calcium nitrate tetrahydrate ($CaNO_3{\cdot}4H_2O$), diammonium hydrogen orthophosphate ($(NH_4)_2HPO_4$), glycine (NH_2CH_2COOH), acrylic acid ($CH_2CHCOOH$) and sodium hydroxide (NaOH). All of the chemicals used were analytical grade, and the aqueous solutions were made by dissolving them in double distilled water. The following outlines the experimental procedure used to synthesise the HAP nanoparticles described in this study. To prepare a transparent precursor for calcium, 1.2 g of calcium nitrate (0.05 mol/l) was dissolved in 100 ml of double distilled water, and 0.4 g of diammonium hydrogen orthophosphate (0.03 mol/l) was dissolved in 100 ml of double distilled water for phosphate precursor. The aqueous solutions of calcium nitrate tetrahydrate and diammonium hydrogen orthophosphate were mixed slowly with constant stirring. The mixture was then placed in a magnetic stirrer for 6 h. The ratio of Ca:P in the mixture was maintained at 1:6. To the above mixture, 0.1 M glycine and 0.1 M acrylic acid were added and carefully mixed using a magnetic stirrer for approximately 24 h at room temperature. The pH of the mixture was adjusted to 9 using sodium hydroxide. A milky white precipitate was obtained, strongly stirred for another 6 h, and then pushed into an ultrasonicator (EN-60US (Microplus)) at a frequency of 28 kHz. The power used was 150 W for 2 h of irradiation in the ultrasonicator. The resulting precipitate was filtered and washed with double distilled water to remove nitrate ions and the organic moieties enclosed in the as-synthesised powder and then dried at approximately 40 °C for 24 h. The dried powder was further heat treated at 550 °C for approximately 5 h.

2.2. Preparation of TiO_2

$Ti(OC_4H_9)_4$ was used as the precursor to Ti. Initially, diethanolamide (3 ml) was dissolved in ethanol (10 ml). $Ti(OC_4H_9)_4$ was added dropwise to the diethanolamide solution and stirred vigorously for 2 h at room temperature. The produced gel was then dried at 110 °C for 24 h, heat treated at 550 °C for 5 h, and ground to obtain TiO_2 nanoparticles.

2.3. Preparation of Pd–TiO_2

A 0.5 g sample of palladium(II) chloride ($PdCl_2$), which was dissolved in 25 ml of ethanol, was added to 7.2 g of TiO_2 solution using the same method as was used for the pure TiO_2. The resulting mixture was stirred for 2 h at room temperature. Finally, the gel was dried at 110 °C for 24 h, heat treated at 550 °C for 5 h, and ground to produce Pd–TiO_2 nanoparticles. The weight% of Pd to TiO_2 was controlled at 3%.

2.4. Preparation of Pd–TiO_2–HAP

A 0.2 g sample of hydroxyapatite was dispersed in 5 ml of *n*-hexane and added to the solution of Pd–TiO_2 using the same method as used for the Pd–TiO_2. The weight% of HAP to TiO_2 was controlled to be 25%. The resulting mixture was stirred for 2 h at room temperature. The gel was dried at 110 °C for 24 h, heat treated at 550 °C for 5 h, and then ground to obtain the Pd–TiO_2–HAP nanoparticles.

2.5. Characterisation techniques

X-ray diffraction (XRD) analysis was performed at room temperature using a Bruker axis D8 under Cu K_α radiation ($\lambda = 1.540$ Å). Specific surface area was calculated from measurements of N_2-adsorption using a Nova 2000 series Chromatech apparatus at 77 K. Before the measurement, all samples were treated under a vacuum at 250 °C for 2 h. The band-gap of the samples was identified by a UV–visible diffuse reflectance spectra (UV–vis-DRS) in air at room temperature in the wavelength range of 200–800 nm using a UV/Vis/NIR spectrophotometer (V-570, JASCO, Japan). Transmission electron microscopy (TEM) was recorded with a JEOL-JEM-1230 microscope. The samples were prepared by suspending the prepared samples in ethanol and ultrasonicating them for 30 min. Then, a small amount was placed on a copper grid and dried before the sample was loaded into the TEM. The X-ray absorption fine structure (XAFS) analysis, X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) were performed at the BL-7C facility of the Photon Factory at the National Laboratory for High-Energy Physics, Tsukuba, Tokyo, Japan. The K-edge XAFS spectra of Pd was measured in the fluorescence mode at 298 K, and the Fourier transformation was performed on K^3-weighted EXAFS oscillations in the range of 1–10 $Å^{-1}$. The amount of palladium in the crystalline samples was obtained by the energy dispersive X-ray technique (Oxford) combined with a scanning electron microscope (JEOL-JSM-5410).

2.6. Analysis of hydroxyl radicals (OH)

The formed −OH radical on the surface is measured by the photoluminescence method, which uses terephthalic acid as a probe molecule. The intensity of the PL signal of 2-hydroxyterephthalic acid, produced by a reaction of terephthalic acid with OH radicals, was measured at 425 nm. Therefore, the amount of OH produced on the surface of TiO_2 is proportional to the PL intensity of 2-hydroxy terephthalic acid. The steps to measure the OH radical on the surface begin with 0.1 g of the prepared sample being dispersed in a terephthalic acid aqueous solution (20 ml, 5×10^{-4} M) with NaOH(2×10^{-3} M) in a dish with a diameter of approximately 9.0 cm. The light source is a 125 W high pressure Hg lamp,